AN INTERLABORATORY STUDY

OF THE

ONTARIO REGULATION 309

LEACHATE EXTRACTION PROCEDURE

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June 1986

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AN INTERLABORATORY STUDY OF THE ONTARIO REGULATION 309 LEACHATE EXTRACTION PROCEDURE

Introduction

One of the definitions of hazardous waste, according to Regulation 309 of the Ontario Environmental Protection Act, is based on the concentrations of selected chemical parameters in a leachate obtained from the waste material. Regulation 309 describes the exact manner in which the leach procedure is to be performed. It also states that individual waste generators and/or their agents are responsible for performing the specified test and providing the Ministry with the information required.

To test the efficacy of the procedure, especially with regard to its precision, the Laboratory Services Branch invited several private laboratories to participate in an interlaboratory study of the leachate extraction and analytical procedure. This report presents some of the findings of the study.

Sample Selection and Description

The Laboratory Services Branch analyses a large variety of samples from different industries in Ontario for leachate toxicity. From this repertoire of samples, five were selected based on their homogeneity and the concentration of selected chemical elements in them. Four samples were chosen to represent high concentrations of elements of interest and one for the concentration at the detection limit of the analytical method used.

The following samples were selected:

- A. Electrostatic Precipitator Dust from a nickel smelting operation; High concentrations of Cd, Cu, Ni, Zn.

 Particle size: less than 5 µ m diameter
- B. Coal Bottom Ash from a power generating plant.
 Low concentrations of metals.
 Particle size: Powdery to approximately 5 mm diameter
- C. Steel Flue Dust from baghouse.

 High concentrations of Cd, Cu, Mn, Pb Zn.

 Particle size: less than 5 µm diameter

- D. Iron Foundry Baghouse Dust.

 High concentrations of Cd, Mn, Pb, Zn.

 Particle size: less than 5 µm diameter
- E. Plating Sludge from pollution control treatment plant.
 High concentrations of Cu, Cr, Mn, Ni.
 Particle size: less than 5 μm diameter

The samples were analysed by the MOE laboratory after digestion with aqua regia. The results which are presented in Table 1, are deemed to indicate the maximum concentration of the target parameter that might be leached. Professor J. Kramer of McMaster University determined the crystalline compounds in the samples by X-ray diffraction. Results shown in Tables 2 to 6, provide some idea of the complexity of the samples.

The number of samples and the parameters chosen were such that an excessive analytical load was not placed on the laboratories, which participated in the study on a voluntary basis. About fifty pounds of each sample were collected by the Ministry's regional staff. Each sample was homogenized by laboratory (8) on a roller mill for a period of four days. The bulk material was then sub-divided into approximately two hundred gram aliquots and submitted to the fifteen participating laboratories for analysis. A reference solution from the United States Environmental Protection Agency was also provided as a control for instrumental calibration standards.

Extraction Procedure and Chemical Analysis

The extraction procedure specified in Regulation 309 is presented in Appendix A. The instrumental methods used were ICP, DCP and AAS. The reporting sheet to submit results (and other pertinent data) to the Ministry laboratory is shown in Appendix B.

Results and Discussion

The results for the samples, reported by the laboratories are presented in Tables 7 to 11. The results for the EPA reference solution are shown in Table 12. For the statistical analysis, the means, standard deviations and relative standard deviations were calculated for all reported values using

a computer program for the HP9825, equipped with a graphics plotter. In a second iteration, values lying outside the range of of \pm 2 standard deviations were discarded and new means, standard deviations and relative standard deviations were calculated. Figures 1, 1a, b, c, d to 5, 5a, b, c, d show the concentration of each element obtained by the corresponding laboratories for each of the five samples respectively. The means and standard deviations are also depicted.

The summary results for the means and relative standard deviations for all values and for those excluding the outliers are presented in Tables 13 to 17.

A major conclusion of this study is that most laboratories are capable of competently performing the Regulation 309 leachate extraction procedure. Column N in Tables 13 - 17 indicate the number of laboratories out of 15 fifteen with results within two standard deviations of the mean. For any single sample, in general, only one laboratory was outside of this range, in the worst case, there were two outliers. When each parameter is considered for all of the samples, there is no parameter that was analysed by all laboratories with results within two standard deviations of the mean, as shown below.

Parameter	Outlier Laboratory Number
рН	5, 6, 9, 13(3x)
Cd	8, 10(2x), 13(2x)
Cu	4 (2x), 7, 9
Cr	3, 4, 8, 10 (3x)
Mn	4, 10, 13
Ni	4, 10(2x), 15
РЬ	4, 10(2x), 15
Zn	4, 13(3x), 15

The three laboratories with the most frequent outliers were laboratory 10 with 9 data points, laboratory 13 with 8 data points and laboratory 4 with 6 data points respectively. Laboratory 13 apparently misunderstood the instructions for pH control and added 4 mL of acetic acid whereas the method calls for 4 mL of acid per gram of sample. One unexpected finding of this study was the significant difference in the amount of acid that was added to any sample to obtain the right pH. For the EPA reference solution, two laboratories reported low values for zinc. This is also reflected in the excluded values for the zinc data in the leachates.

There are no indications of instrumental biases (ICP, AAS), nor that one element could be analysed more precisely than any other. Differences were reported in detection limits but these, again, do not seem to be instrument related. Several laboratories encountered difficulties (reflected in the large RSD's) in analysing lead in the steel flue dust and in the iron foundry dust leachate, as a white precipitate was formed on standing. X-ray diffraction analysis (MOE lab) determined the precipitate to be ankerite, PbSO4. This precipitate could be dissolved by nitric acid treatment of the leachate, which some laboratories did. It would be a good analytical practice to treat all leachate samples with a nitric acid digestion. The official procedure does not require this to be done, at the present time, but it may be amended in the future.

With the impending implementation of Regulation 309, many diverse types of waste materials will need to be tested for leachate toxicity. This study reveals that for the most common types of wastes, analytical facilities in the province for metal analyses will provide reliable data. For certain sample types obtaining a representative sample is expected to be a greater source of uncertainty than the chemical analysis.

AUTHOR'S NOTE

The data obtained in this study may be interpreted in other ways than the one chosen by the author. Readers are welcome to use all data published here for alternative statistical treatments.

TABLE 1
(Results in %)

Aqua Regia Acid Digestion, ICP Analysis of Samples

Sample	A	В	С	D	E
Moisture	0.50	0.80	0.40	1.20	68.00
LOI	17.70	12.30	8.50	15.20	28.50
Cu	6.20	0.01	0.26	0.27	9.31
Ni	2.70	ND*	0.03	0.01	4.30
Zn	0.07	ND	12.50	8.68	0.04
Cd	ND	ND	0.04	0.02	ND
Co	0.12	ND	0.01	ND	ND
Cr	0.04	0.01	0.30	0.03	16.21
Pb	0.02	ND	2.65	15.75	0.05
Fe	42.00	10.40	36.50	8.20	1.00
Mn	0.03	0.04	4.32	1.35	0.02
Al	0.07	2.30	0.35	0.86	1.33
Ca	0.15	1.00	4.20	0.90	3.58
Mg	0.82	0.10	2.71	1.25	0.70
Na	0.06	0.05	0.56	0.54	1.52
K	0.30	0.01	2.30	1.80	1.30
P	0.06	0.02	0.31	0.35	0.10
C**	0.10	7.10	0.69	12.48	1.12
S**	9.80	1.32	0.55	1.68	11.30
Si***	4.90	15.75	2.27		3.16

^{*} ND not detected

^{**} Leco induction furnace

^{***} XRF Analysis

TABLE 2

X-Ray Diffraction Data *

SMELTER ESP DUST

SAMPLE A:

(Name, composition)	(d-spacing in	decreasing	g intensity)	
Magnetite (Fe ₃ 0 ₄)	2.53	1.49	2.97	1.62	2.10
Hematite (Fe ₂ 0 ₃)	2.70	2.50	1.70	3.69	1.49
Chlorite (Mg-Fe-Al-0-OH silicate)	4.77	14.0	7.14		
Yugawaralite (CaAl ₂ Si ₈ O ₁₆ .4H ₂ O)	5.82	4.68	3.06		
Pyrite (FeS ₂)	1.63	2.71	2.43	1.92	1.45
Tenorite (CuO)	2.52	2.32	2.53	1.51	
Bunsensite (NiO)	2.09	2.41	1.48		
Villamaninite (Cu,Fe,Ni S ₂)?	2.85	1.72	2.55		
Violarite (Ni,Fe 3S4)?	5.82	4.68	3.06		

Other possibilities in small amounts are: silicates - actinolite, biotite, forsterite, phlogopite, quartz; chalcopyrite(Cu,FeS₂), covellite((CuS),cuprite(CuO)

(underlined values represent major intensities found)

^{*} X-ray data, courtesy Professor James Kramer, McMaster University, Hamilton

TABLE 3

X-ray Diffraction Data *

COAL BOTTOM ASH

SAMPLE B:

(Name, composition)	(d-	spacing in	decreasing	intensity)		
Hydrated Ca-silicates	2.95 1.69	4.35 5.44	9.5 <u>3.04</u>			
Dickite (Al ₂ Si ₂ O ₅ (OH) ₄)	7.15	3.58	2.33	2.51		
Graphite (C)	3.36	2.0	1.67			
Gypsum (CaSO ₄ ,2H ₂ O)	2.56	3.06	4.27	2.68	2.87	3.79
Halloysite (Al ₂ Si ₂ O ₅ (OH) ₄)	7.50	3.63	4.42	2.56	1.68	
Hematite (Fe ₂ O ₃)	2.70	2.52	1.70	3.69	1.49	
Magnetite (Fe ₃ O ₄)	2.53	1.49	2.97	1.62	2.10	
Mullite (Al ₆ Si ₂ O ₁₃)	3.39	3.43	2.21			
Nontronite (NaFe ₂ Si ₄ O ₁₀ (OH) ₂)	13.3	4.51	3.49			
Pyrite (FeS ₂)	1.63	2.71	2.43			
Quartz (SiO ₂)	3.34	4.26	1.82			
Sillimanite (Al ₆ Si ₂ O ₁₃)	3.36	2.20	3.41			

(underlined value represent major intensities found)

^{*} X-ray data, courtesy Professor James Kramer, McMaster Univerity, Hamilton

TABLE 4

X-ray Diffraction Data *

STEEL FLUE DUST

SAMPLE C

(Name, composition)

(d-spacing in decreasing intensity)

Beta Mn Fe	2.09	1.99	1.90		
Epsilon Zn Fe	2.11	2.58	1.90		
Franklinite (ZnFe ₂ O ₄)	2.52	2.98	1.48		
Galena (PbS)	2.97	3.43	2.10		
Hematite (Fe ₂ O ₃)	2.70	2.52	1.70	3.69	1.49
Kempite (Mn ₂ (OH) ₃ Cl)	<u>5.70</u>	5.36	2.39	1.69	2.97
Larsenite (PbZnSiO ₄)	3.19	2.85	1.49		
Lead (Pb)	2.86	2.48	1.49		
Litharge (PbO)	3.12	2.81	1.87	1.68	2.51
Magnetite (Fe ₃ O ₄)	2.53	1.49	2.97	1.62	2.10
Plumboferrite (PbFe _{4O7})	2.64	2.81	2.96	3.90	1.68
Zincite (ZnO)	2.48	2.82	2.60		

(underlined values represent major intensities)

^{*} X-ray data, courtesy Professor James Kramer, McMaster University, Hamilton

TABLE 5

X-ray Diffraction Data *

SAMPLE D IRON FOUNDRY DUST

(Name, composition)	(d-spacing in decreasing intensity)								
Bustamite (Ca,Mn)3Si3O9) Coronadite (PbMn7O14)	2.24 3.10	3.72 3.47	3.23 1.54	2.64					
Franklinite (ZnFe ₂ O ₄) Hematite (Fe ₂ O ₃) Larsenite (Pb,Zn SiO ₄)	2.54 2.70 3.19	2.98 2.50 2.85	1.49 1.70 4.88	3.69	1.49				
Magnetite (Fe ₃ O ₄)	2.53	1.49	2.97	1.62	2.10				
Massicot (PbO) Plumbo-ferrite (PbFe ₄ O ₇)	3.07 2.64	2.95 2.81	2.74 2.96	1.85 3.90	1.64				
Pyrolusite (MnO ₂) Quartz (SiO ₂)	3.11 3.34	2.41 4.26	1.62 1.82						

(underlined values represent major intensities)

^{*} X-ray data, courtesy Professor James Kramer, McMaster University, Hamilton

TABLE 6
X-ray Diffraction Data *

SAMPLE E

PLATING SLUDGE

(Name, composition)	(d-spacing	-spacing in decreasing intensity)								
Chalcocyanite (CuSO ₄)	<u>3.55</u>	2.61	4.19							
Copper Hydroxide Cu(OH) ₂	<u>3.75</u>	2.64	2.26							
Kainite (KMg(SO ₄) ₂ (OH)6.3H ₂ O)	7.37	3.08	7.77	8.12	3.03					
Lime (CaO)	2.41	1.70	2.78	1.45						
Morenosite (NiSO ₄ .7H ₂ O)	4.20	5.30	2.85	3.45	2.65					
Nakaurite (Cug(SO ₄) (CO ₃) OH) ₆ .48H ₂ O)	2.37	7.31	3.65	1.91						
Nickel Hydroxide Ni(OH) ₂	4.53	2.32	2.68							

(underlined values represent major intensities)

^{*} X-ray data, courtesy Professor James Kramer, McMaster University, Hamilton

TABLE 7

SAMPLE A SMELTER ESP DUST

Lab.#	Instrument	Initial pH	Final pH	Acid added mL	Cd	Cu	Cr	Mn mg/L	Ni		Pb	Zn
ĺ.	AAS	3.75	3.35	0	0.360	847	< 0.01	3.94	63.90	<	0.05	8.56
2.	AAS	3.36	3.27	0	0.240	834	0.04	3.71	79.00	<	0.03	9.11
3.	AAS	3.60	3.50	0	0.300	1065	1.10	4.40	90.00		0.10	8.30
4.	AAS/ICP	3.50	3.30	0	0.305	2115	< 0.10	6.75	110.00	<	0.10	11.40
5.	AAS	3.50	2.82	0	0.260	765	< 0.05	4.21	77.60		0.40	9.20
6.	AAS	3.30	3.30	0	0.240	891	< 0.02	4.60	77.00	<	0.02	8.25
7.	AAS	3.76	3.62	0	0.270	830	< 0.08	4.30	84.00	<	0.13	9.00
8.	AAS/DCP	3.69	3.26	0	0.455	975	< 0.02	4.46	82.38		0.20	9.11
9.	AAS	3.73	3.51	0	0.270	850	< 0.06	4.50	72.00		0.57	9.30
10.	ICP	3.50	3.20	0	5.000	1200	< 1.00	5.00	91.00	<	3.00	5.00
11.	AAS	3.65	3.52	0	0.260	814	0.02	4.78	70.00		0.05	9.02
12.	ICP	3.65	3.37	0	0.273	1100	< 0.01	5.70	91.00		0.09	9.10
13.	ICP	3.82	3.76	0	0.170	792	< 0.01	4.92	76.00	<	0.05	< 0.05
14.	AAS	3.74	3.45	o	0.259	873	0.06	3.70	82.00	<	0.07	8.24
15.	AAS	3.80	3.40	0	0.330	830	0.08	4.50	100.00		0.50	0.82

Hell)

TABLE 8 SAMPLE B COAL BOTTOM ASH

Lab.#	Instrument	Initial pH	Final pH	Acid added mL	Cd	9	Cu	Cr	Mn mg/L	Ni		Pb	Z	^Z n
1.	AAS	4.15	4.15	0	0.030		0.14	< 0.010	1.08	0.10	<	0.05		0.19
2.	AAS	3.50	4.07	0	<0.020		0.18	< 0.020	0.78	0.06	<	0.03		0.17
3.	AAS	4.50	5.00	0	0.007		0.03	< 0.020	0.80	0.07		0.06		0.08
4.	ICP/AAS	4.00	4.45	0	0.010	<	0.10	< 0.100	1.05	0.10		0.10		0.25
5.	AAS	3.84	4.30	0	<0.010	<	0.10	< 0.050	0.88	< 0.10	<	0.05		0.10
6.	AAS	4.10	4.10	0	<0.010	<	0.02	< 0.020	0.74	< 0.02	<	0.04		0.16
7.	AAS	4.21	4.46	0	<0.010		0.24	< 0.080	1.10	0.04	<	0.13		0.09
8.	AAS/DCP	4.11	4.39	0	0.045	<	0.03	< 0.025	0.83	0.07		0.30		0.22
9.	AAS	4.37	6.24	0	<0.010	<	0.03	< 0.060	0.61	< 0.06	<	0.01		0.04
10.	ICP	3.70	4.50	0	<0.020	<	0.02	< 0.020	1.00	< 0.05	<	0.03		0.06
11.	AAS	4.20	4.40	0	<0.005	<	0.01	< 0.005	0.55	0.04	<	0.02		0.07
12.	ICP	4.13	5.68	0	<0.004		0.08	< 0.02	0.72	0.04	<	0.06		0.06
13.	ICP	4.02	4.59	0	0.010		0.06	< 0.010	1.01	0.08	<	0.05	<	0.05
14.	AAS	3.95	4.33	0	<0.005		0.03	< 0.008	0.66	< 0.04	<	0.07		0.11
15.	AAS	4.20	4.30	0	0.020		0.03	< 0.010	1.00	0.41		0.37		0.09

TABLE 9
SAMPLE C STEEL FLUE DUST

											•
Lab. #	Instrument	Initial pH	Final pH	Acid added mL	Cd	Cu	Cr	Mn mg/L	Ni	Pb	Zn
1.	AAS	8.05	6.50	100	12.70	1.67	0.03	56.00	0.34	61.00	1680
2.	AAS	5.85	6.26	200	14.00	1.07	0.02	58.00	0.27	32.00	1639
3.	AAS	8.60	6.70	180	14.00	1.60	0.03	62.00	0.20	41.00	1442
4.	AAS/ACP	7.30	6.15	200	10.00	4.95	< 0.10	62.50	0.20	198.50	2395
5.	AAS	7.07	6.19	400	13.50	1.10	< 0.05	60.30	0.20	158.00	1600
6.	AAS	7.80	5.70	200	12.20	4.12	< 0.02	51.00	0.14	30.60	1000
7.	AAS	7.77	6.51	200	15.00	1.20	< 0.08	62.00	0.16	140.00	1700
8.	AAS/DCP	7.36	6.59	200	15.32	1.51	< 0.03	67.00	0.26	38.00	1995
9.	AAS	8.04	6.57	200	14.00	1.92	< 0.06	57.50	0.21	30.00	1700
10.	ICP	7.35	6.50	58	12.50	2.00	< 1.00	19.50	5.00	27.00	350
11.	AAS	8.00	6.35	200	14.80	3.48	0.02	63.00	0.28	78.00	1690
12.	ICP	8.26	6.58	200	15.00	2.10	0.10	68.00	0.23	110.00	1800
13.	ICP	6.40	7.14	4	2.20	0.09	< 0.01	24.00	< 0.05	0.50	< 0.05
14.	AAS	6.74	6.57	200	14.04	1.77	0.05	66.40	0.25	34.90	1770
15.	AAS	7.00	6.30	164	13.00	1.74	0.02	45.00	0.53	96.60	1200

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TABLE 10
SAMPLE D IRON FOUNDRY DUST

Lab.#	Instrument	Initial pH	Final pH	Acid added mL	Cd		Cu Cr		Mn mg/L	Ni	Pb	Zn
1.	AAS	6.80	5.35	56	3.81		0.55	0.02	60.60	0.36	53.0	977
2.	AAS	5.49	5.02	159	4.26		0.34	0.02	73.00	0.40	215.0	1118
3.	AAS	6.95	5.15	143	5.46	<	0.02	0.45	99.00	0.45	333.0	1380
4.	AAS/ICP	6.20	5.15	200	4.35		0.25	< 0.10	115.50	0.30	727.5	2060
5.	AAS	6.48	5.05	NR	4.92		0.40	< 0.05	83.40	0.40	480.0	1360
6.	AAS	7.00	5.20	100	3.25		0.06	< 0.02	60.00	0.26	87.3	762
7.	AAS	6.36	5.73	82	4.00		0.06	< 0.08	56.00	0.23	110.0	890
8.	AAS/DCP	6.27	5.25	127	4.59		0.19	< 0.03	68.75	0.43	242.5	1118
9.	AAS	6.79	5.05	200	4.90		0.75	< 0.06	80.00	0.38	215.0	1390
10	ICP	6.50	6.10	54	6.00	<	1.00	< 1.00	65.00	< 5.00	30.0	950
11.	AAS	6.85	5.00	181	5.02		0.48	0.01	84.00	0.41	87.0	1290
12.	ICP	7.07	5.06	200	5.80		1.00	0.10	100.00	0.40	560.0	1600
13.	ICP	5.98	6.46	4	2.12		0.04	0.01	31.90	0.14	5.3	< 0.05
14.	AAS	6.56	5.15	200	4.75		0.02	0.06	102.70	0.40	756.0	1440
15.	AAS	6.30	5.60	70	3.40		0.01	0.01	41.00	0.51	54.5	760

NR = Not Reported

TABLE 11
SAMPLE E PLATING SLUDGE

Lab.#	Instrument	Initial pH	Final pH	Acid added mL	Cd	Cu	Cr	Mn mg/L	Ni		Pb	Zn
1.	AAS	7.73	5.60	90	0.010	10.51	9.08	1.18	51.20		0.05	0.56
2.	AAS	6.75	5.27	200	<0.020	31.00	17.00	0.83	78.00		0.18	0.45
3.	AAS	7.80	5.20	87	0.011	52.00	37.00	0.71	78.00	<	0.05	0.46
4.	AAS/ICP	6.70	5.30	200	<0.010	20.70	12.80	1.35	65.00	<	0.10	0.15
5.	AAS	6.60	5.07	NR	<0.010	21.30	10.43	1.04	5.90		0.40	0.50
6.	AAS	8.30	5.40	175	<0.010	12.40	10.80	1.00	55.00	<	0.04	0.75
7.	AAS	7.45	5.32	200	<0.010	48.00	26.00	1.60	100.00		0.58	0.65
8.	AAS/DCP	7.36	5.20	200	0.050	36.55	40.50	1.72	101.25		0.51	0.75
9.	AAS	7.71	5.18	200	<0.010	70.00	20.30	1.48	106.00		0.32	0.56
10.	ICP	7.00	5.50	148	2.000	35.00	20.00	2.00	100.00		2.00 <	1.00
11.	AAS	7.20	5.00	193	0.040	40.10	26.50	1.54	73.00		0.05	0.66
12.	ICP	8.10	5.31	200	0.010	34.00	16.00	1.80	90.00		0.80	0.48
13.	ICP	6.97	7.02	4	0.010	0.11	0.17	< 0.01	0.36	<	0.05 <	0.05
14.	ICP	7.28	5.40	200	<0.005	29.20	16.73	1.24	81.90		1.92	4.25
15.	AAS	7.70	5.70	72	0.010	2.30	0.47	0.73	22.40		0.52 <	0.01

NR = not reported

TABLE 12

SAMPLE EPA REFERENCE SOLUTION

Lab.#	Instrument	Cd	Cu	Cr	Mn mg/L	Ni	Pb	Zn
1.	AAS	0.25	1.32	1.65	1.80	1.10	1.90	1.89
2.	AAS	0.25	1.36	0.84	1.84	1.30	1.65	1.56
3.	AAS	1.0	1.5	1.2	2.0	1.2	1.7	0.125
4.	AAS/ICP	0.23	1.4	1.1	2.5	1.3	1.5	1.3
5.	AAS	0.26	1.4	1.00	1.92	1.1	1.74	1.6
6.	AAS	0.23	0.94	0.96	2.0	1.15	1.63	1.36
7.	AAS	0.27	1.4	1.1	2.0	1.2	1.6	1.7
8.	AAS/DCP	0.26	1.44	0.99	1.83	1.12	1.50	1.55
9.	AAS	0.27	1.55	1.05	1.77	1.18	1.47	1.65
10.	ICP			NOT RE	PORTED			
11.	AAS	0.28	1.40	1.05	2.00	1.12	1.60	1.51
12.	ICb	0.285	1.55	0.99	2.12	1.24	1.62	1.64
13.	ICP	0.27	1.39	1.02	2.03	1.11	1.55	< .05
14.	AAS	0.268	1.493	0.881	2.007	1.26	2.36	1.412
15.	AAS	0.28	1.41	0.95	1.7	1.53	1.45	2.7
Expected	Value	0.280	1.40	1.00	2.00	1.20	1.60	1.60

SAMPLE A SMELTER ESP DUST
MEANS AND RELATIVE STANDARD DEVIATIONS
(mg/L except pH)

All Values			Less Outli		
Paramete	r		(<u>+</u> 2SD)		
	Mean	RSD%	Mean	RSD%	N
рН	3.38	6.3	3.42	4.5	14
Cd	0.599	203.3	0.285	23.2	14
Cu	985.4	34.2	904.7	14.4	14
Cr	0.177	200.7	0.043	71.9	13
Mn	4.63	16.8	4.48	11.8	14
Ni	83.06	14.3	81.13	11.9	14
Pb	0.357	210.5	0.169	108.6	14
Zn	7.63	41.8	8.74	15.8	14

SAMPLE B COAL BOTTOM ASH
MEANS AND RELATIVE STANDARD DEVIATIONS
(mg/L except pH)

	All Values		lues	Less Outlie	ers		
Parameter				(<u>+</u> 2SD)			
		Mean	RSD%	Mean	RSD%	N	
			l•8				
	рН	4.60	13.2	4.48	9.3	14	
	Cd	0.014	77.2	0.012	61.2	14	
	Cu	0.073	92.8	0.073	92.8	14	
	Cr	0.031	94.0	0.026	86.5	14	
	Mn	0.854	20.9	0.854	20.9	15	
	Ni `	0.085	109.1	0.062	41.5	14	
	Pb	0.091	114.2	0.054	60.4	14	
	Zn	0.117	56.9	0.108	53.6	15	

TABLE 15
SAMPLE C STEEL FLUE DUST
MEANS AND RELATIVE STANDARD DEVIATIONS
(mg/L except pH)

All Values			Less Outliers		
Paramet	ter		(<u>+</u> 2SD)		
	Mean	RSD%	Mean	RSD%	N
			3		
рН	6.44	4.9	6.44	2.7	13
Cd	13.15	26.7	13.93	13.2	14
Cu	2.02	62.0	1.81	54.8	14
Cr	0.11	232.5	0.04	71.3	14
Mn	54.81	26.9	59.90	10.9	13
Ni	0.56	222.5	0.24	46.1	14
Pb	71.74	79.8	62.69	75.0	14
Zn	1464	41.9	1568	30.6	14

TABLE 16
SAMPLE D IRON FOUNDRY DUST
MEANS AND RELATIVE STANDARD DEVIATIONS
(mg/L except pH)

All Va		alues Less Outliers			
Param	neter		(<u>+</u> 2SD)		
	Mean	RSD%	Mean	RSD%	Ν
×					
рН	5,35	8.0	5.27	6.1	14
Cd	4.44	23.1	4.61	18.0	14
Cu	0.35	100.9	0.35	100.9	15
Cr	0.13	195.8	0.07	156.2	14
Mn	74.72	31.5	74.72	31.5	15
Ni	0.67	178.9	0.36	26.9	14
РЬ	263.74	96.0	228.58	96.9	15
Zn	1139	41.0	1156	23.7	13

TABLE 17

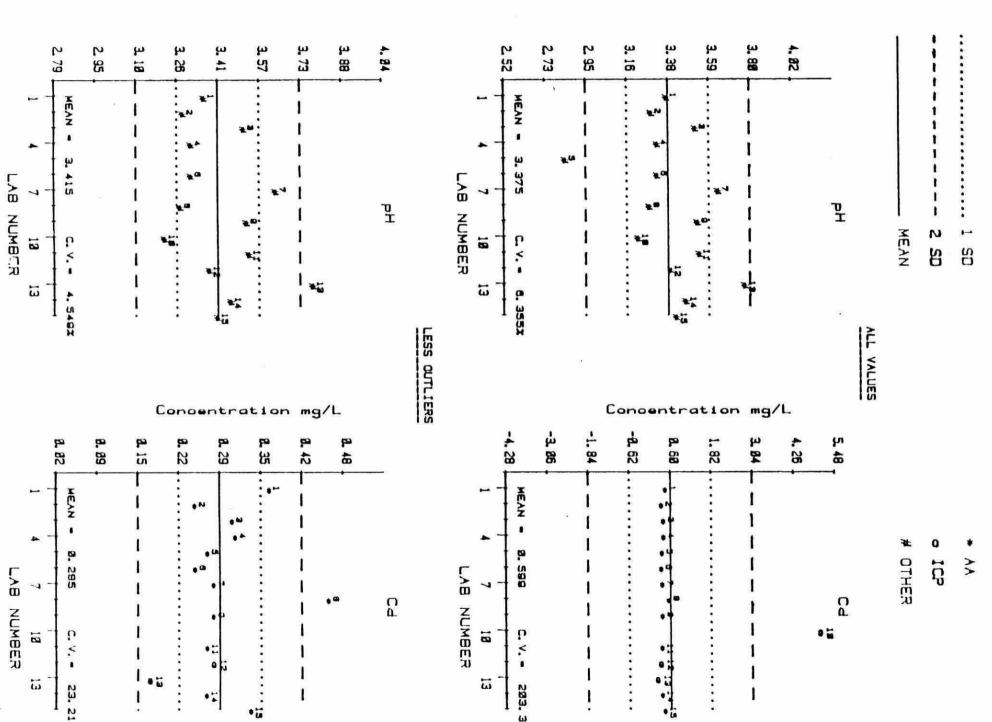
SAMPLE E PLATING SLUDGE

MEANS AND RELATIVE STANDARD DEVIATIONS

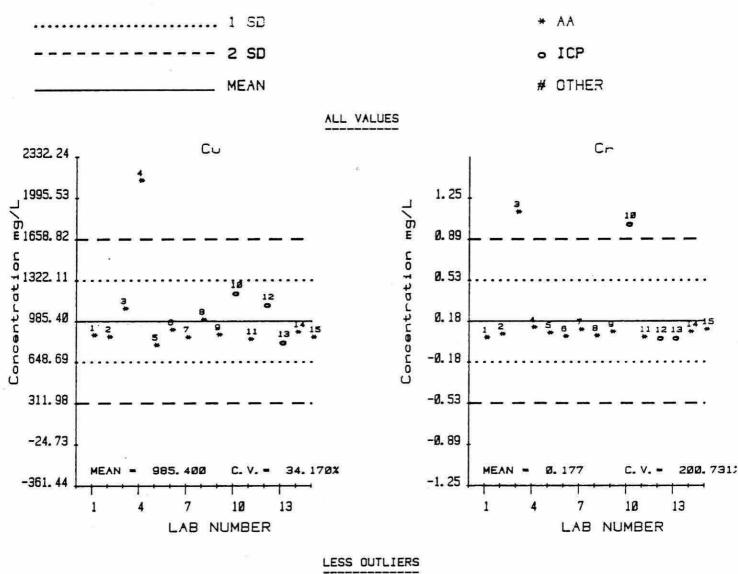
(mg/L except pH)

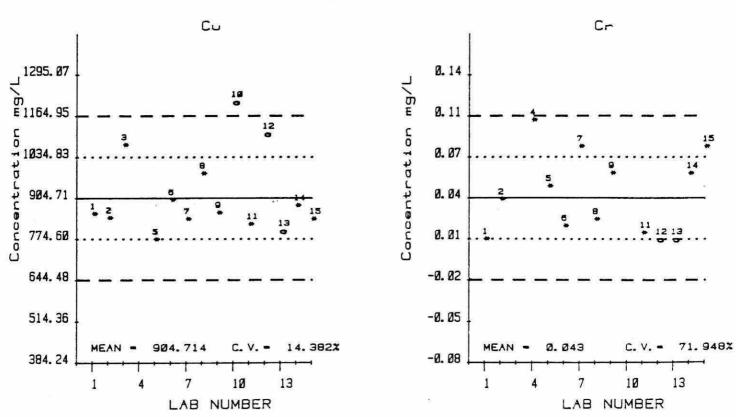
All Values		lues	Less Outliers		
Para	neter		(<u>+</u> 2SD)		
	Mean	RSD%	Mean	RSD%	N
рН	5.43	8.8	5.31	3.5	14
Cd	0.15	346.9	0.02	84.6	14
Cu	29.55	64.6	26.66	60.2	14
Cr	17.59	65.5	15.95	62.6	14
Mn	1.22	42.5	1.30	31.4	14
Ni	67.2	51.0	67.20	51.0	15
Pb	0.51	126.3	0.28	91.9	13
Zn	0.75	133.4	0.50	55.2	14

SMELTER ESP DUST

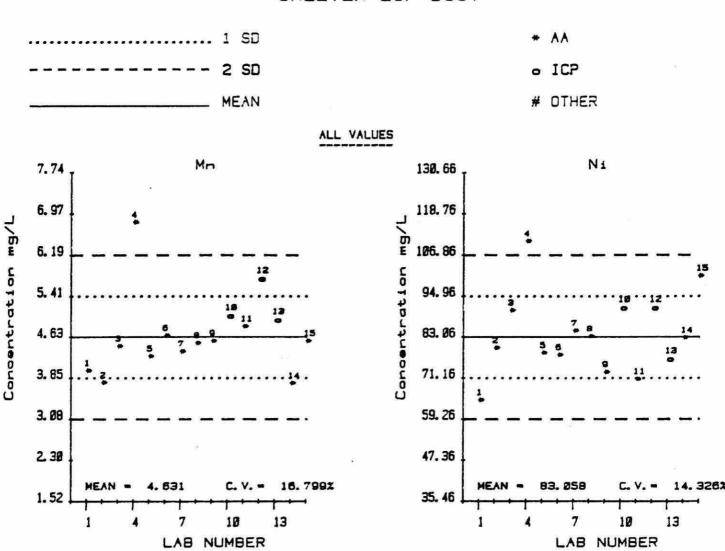


SMELTER ESP DUST

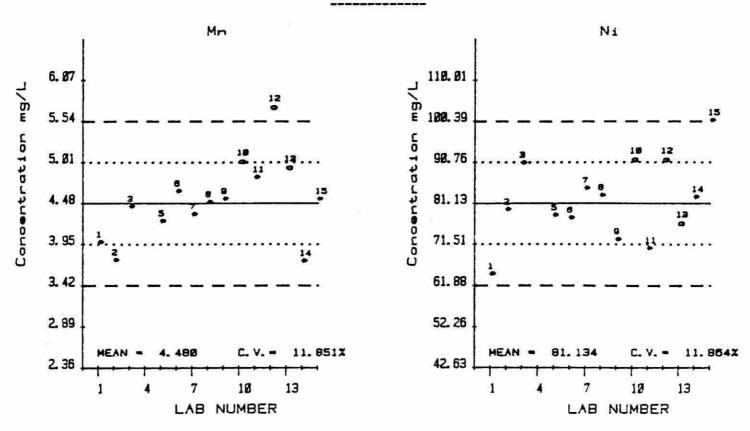




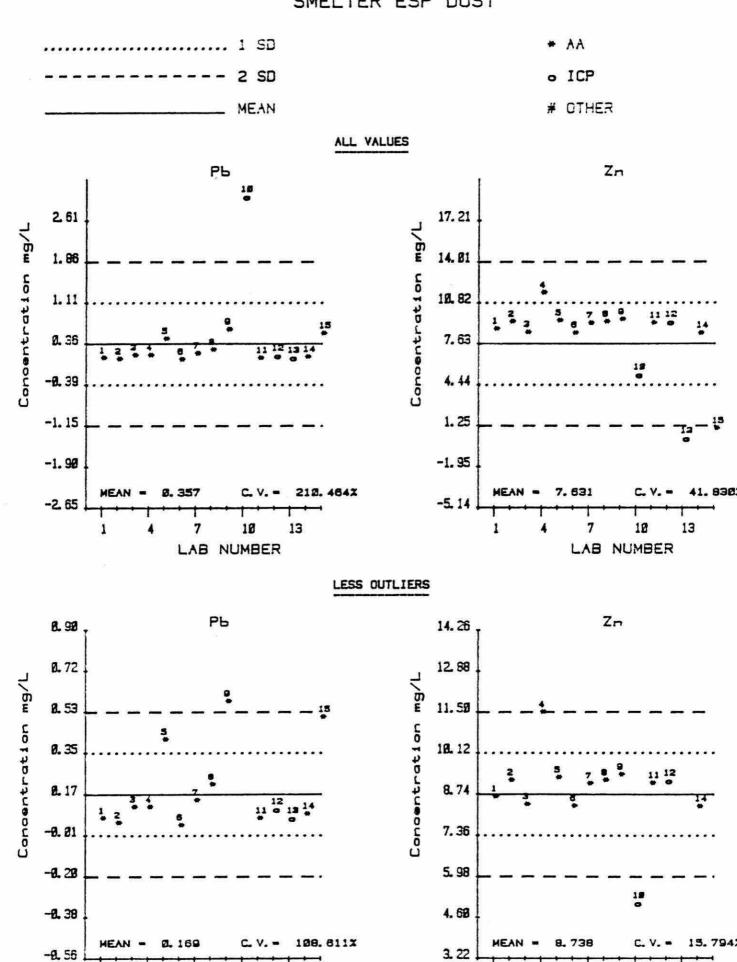
SMELTER ESP DUST



LESS OUTLIERS



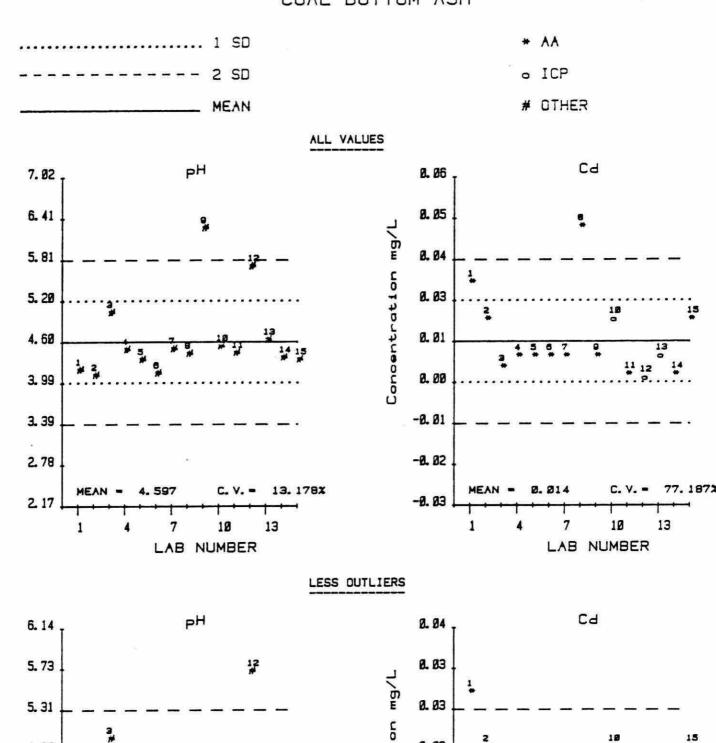
SMELTER ESP DUST

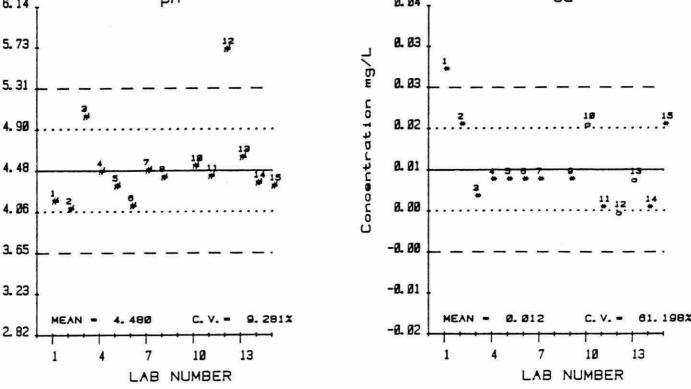


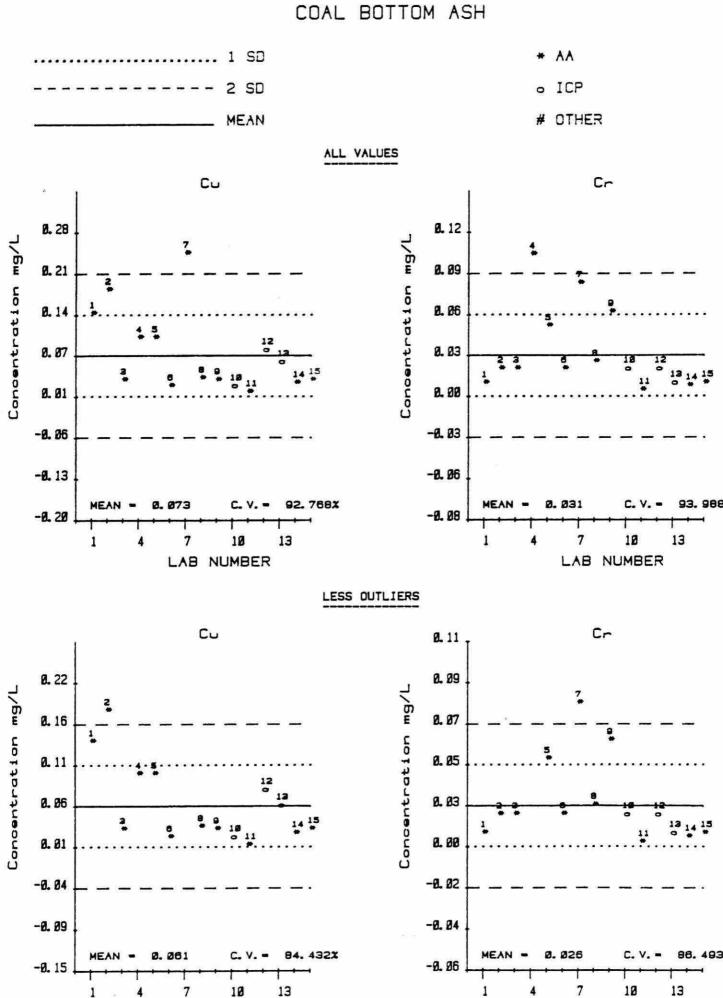
LAB NUMBER

LAB NUMBER

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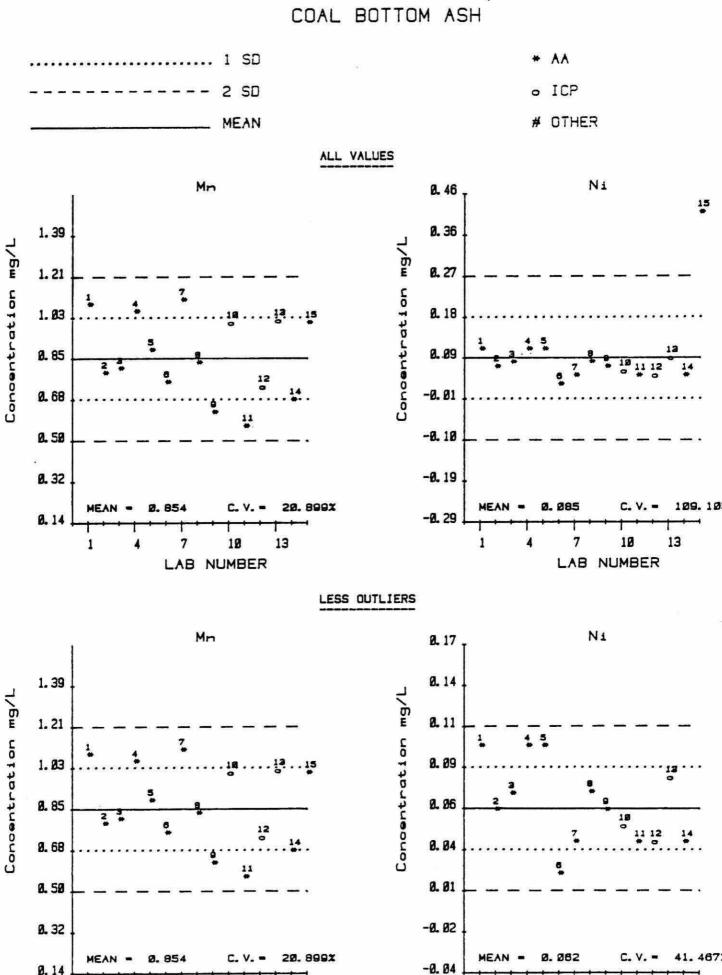






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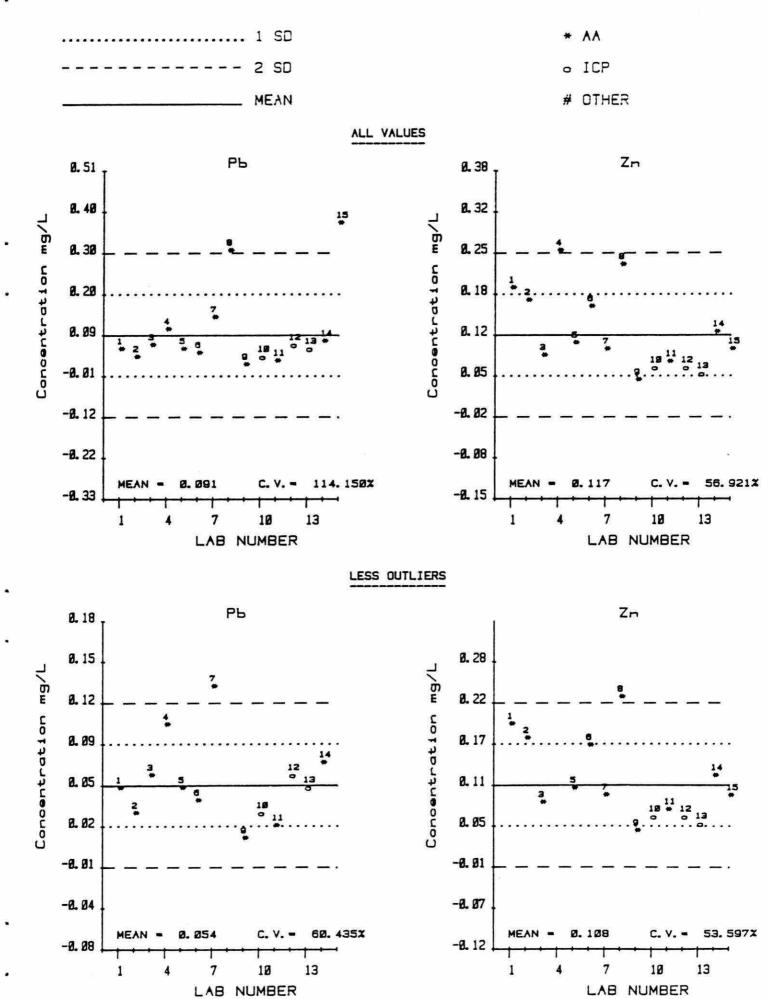
LAE NUMBER



LAB NUMBER

LAB NUMBER

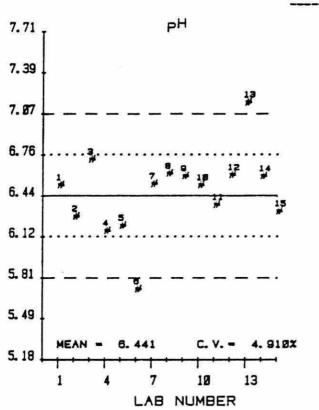
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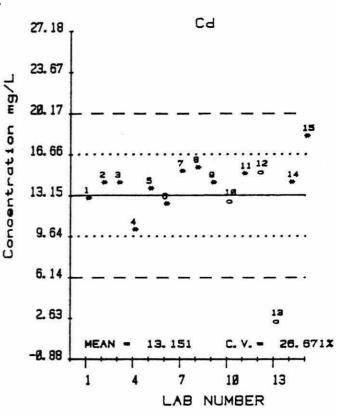


STEEL FLUE DUST

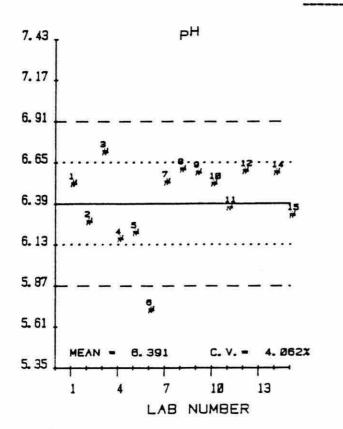


ALL VALUES





LESS OUTLIERS



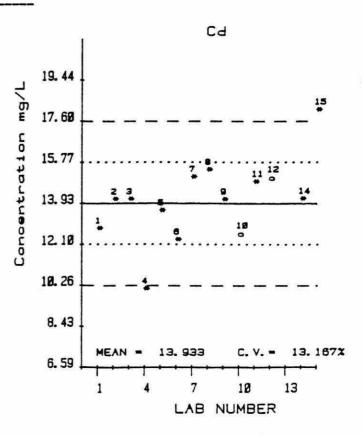
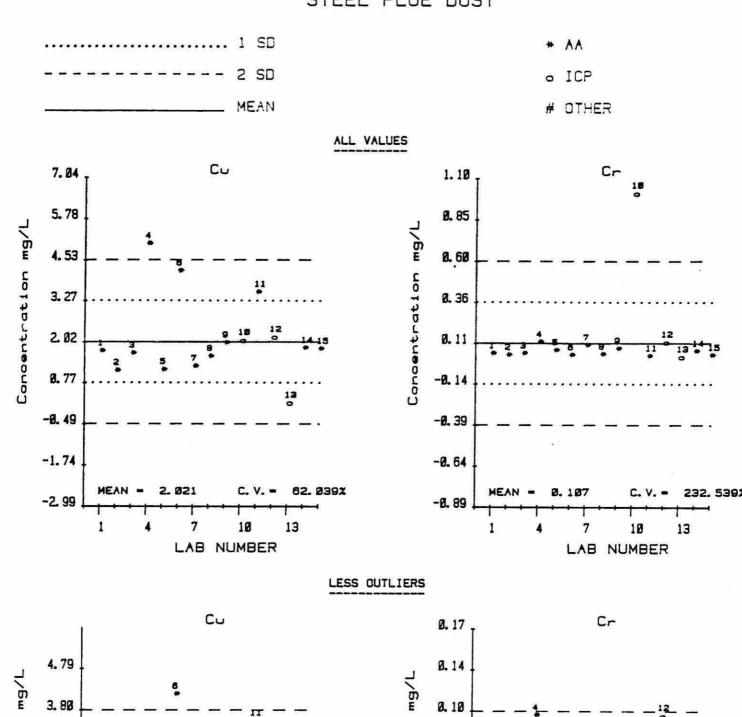
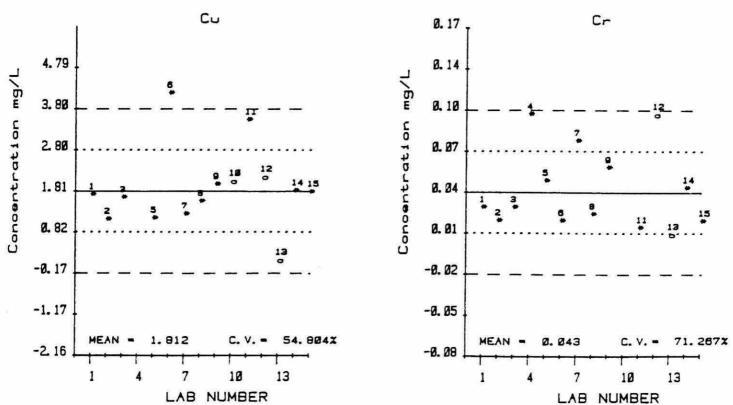
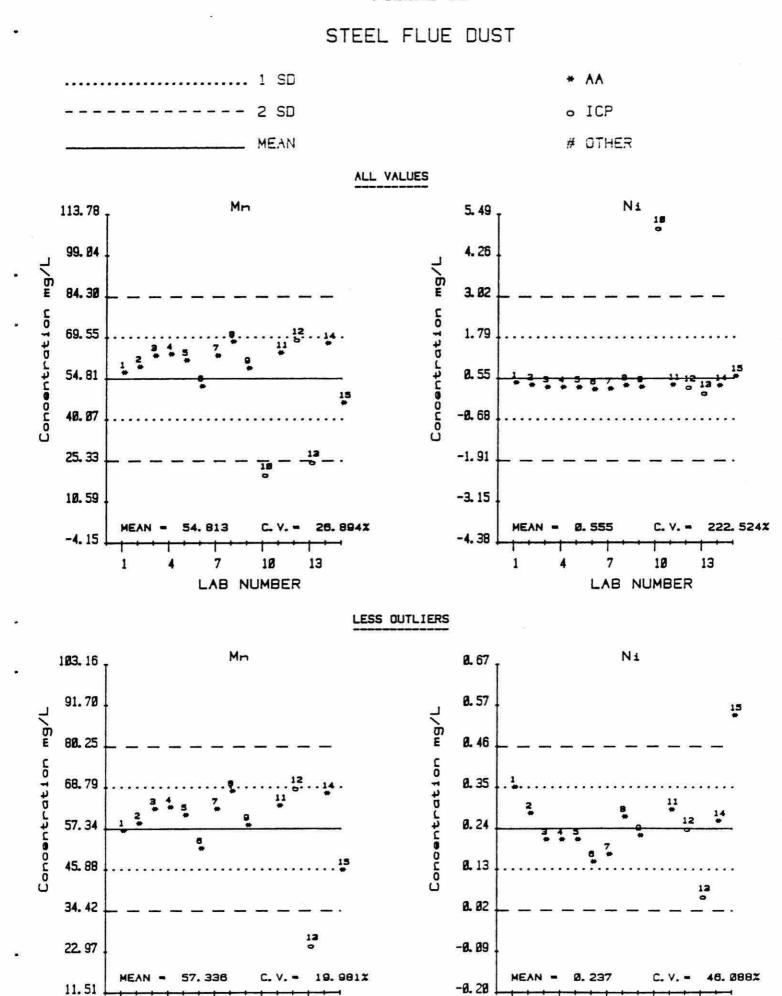


FIGURE 3A

STEEL FLUE DUST







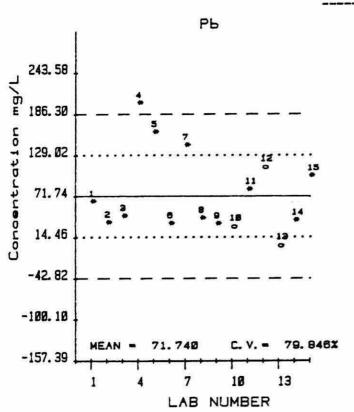
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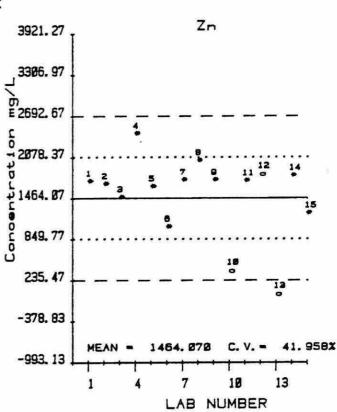
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STEEL FLUE DUST

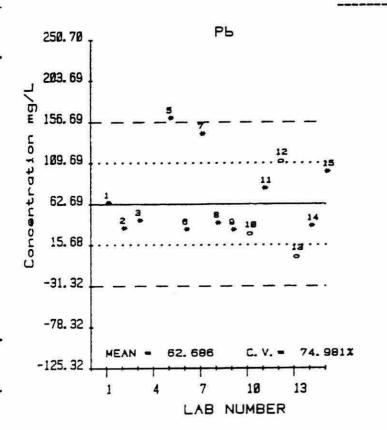


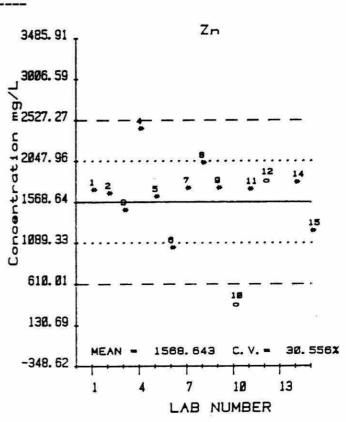
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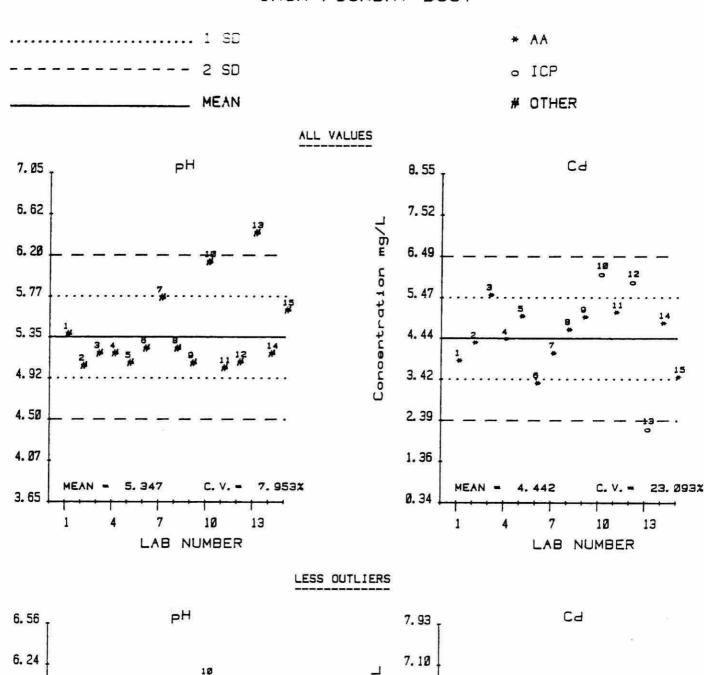


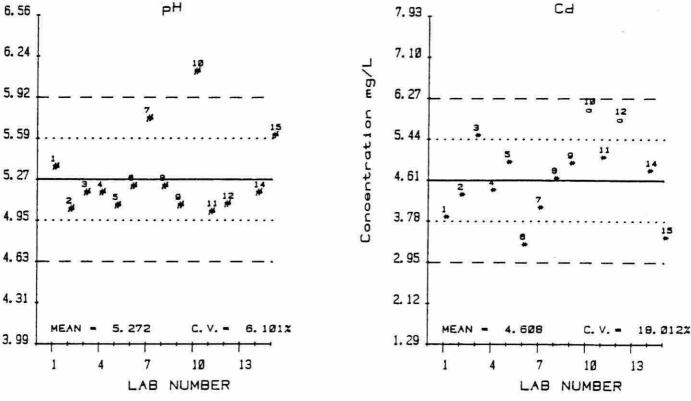


LESS OUTLIERS

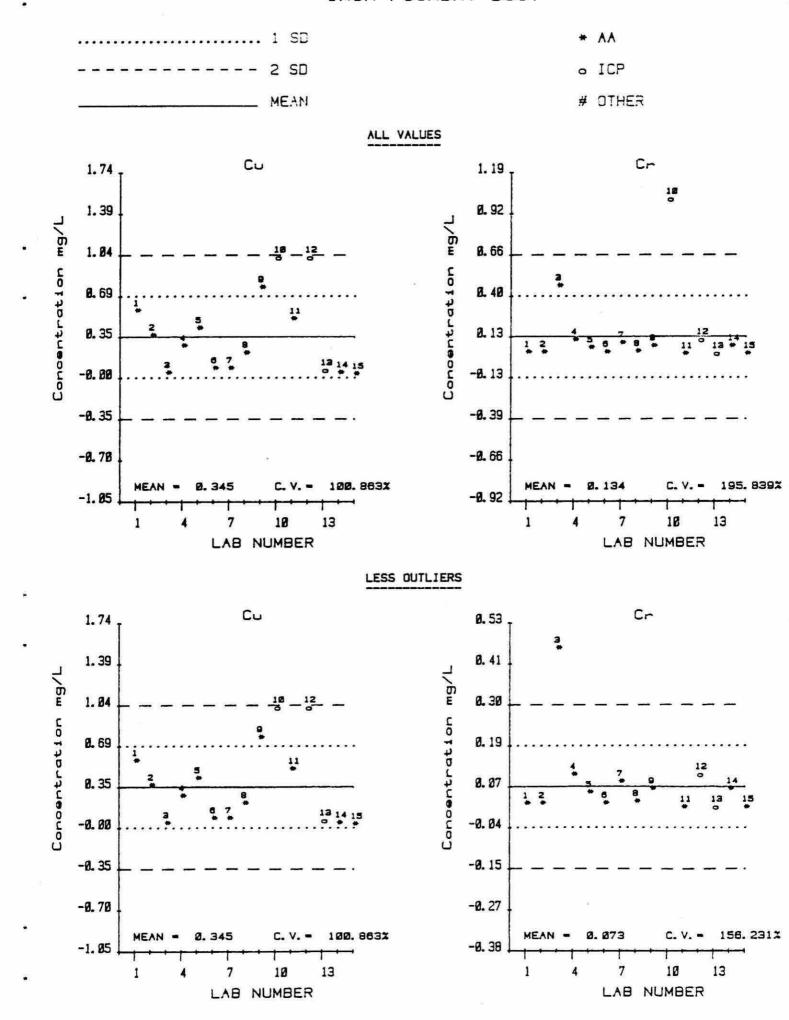




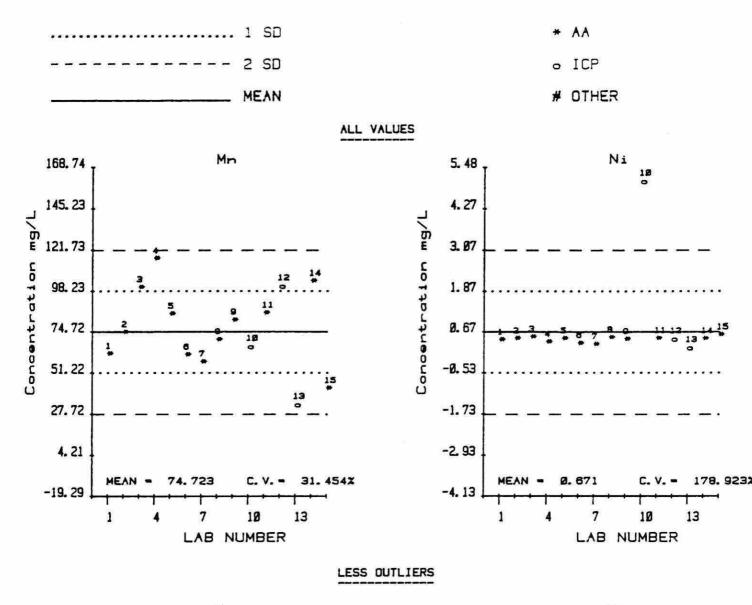


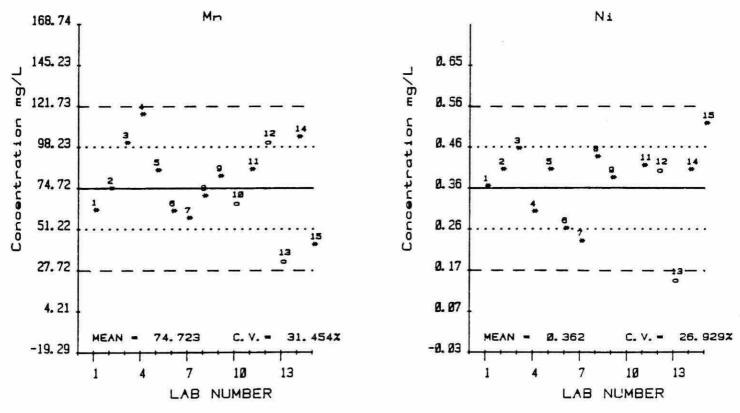


IRON FOUNDRY DUST

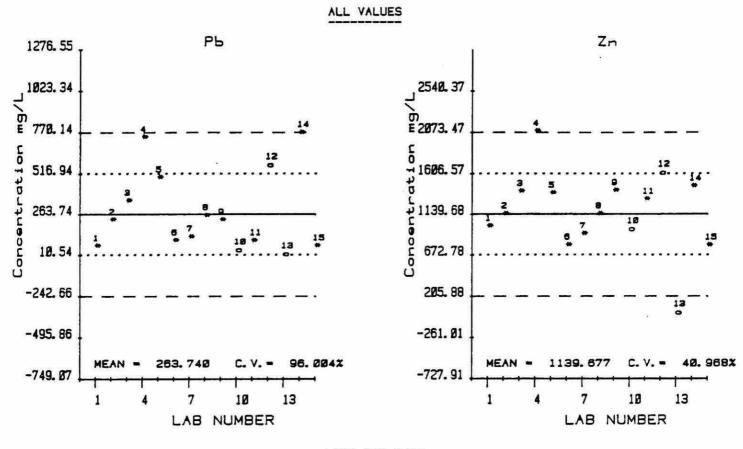


IRON FOUNDRY DUST

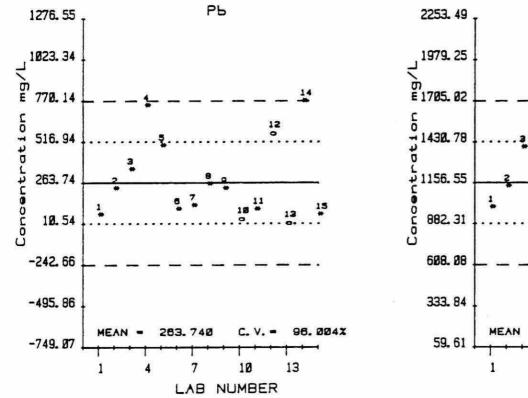


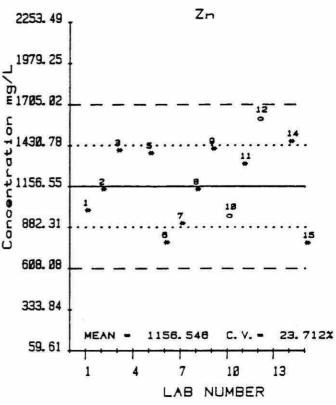


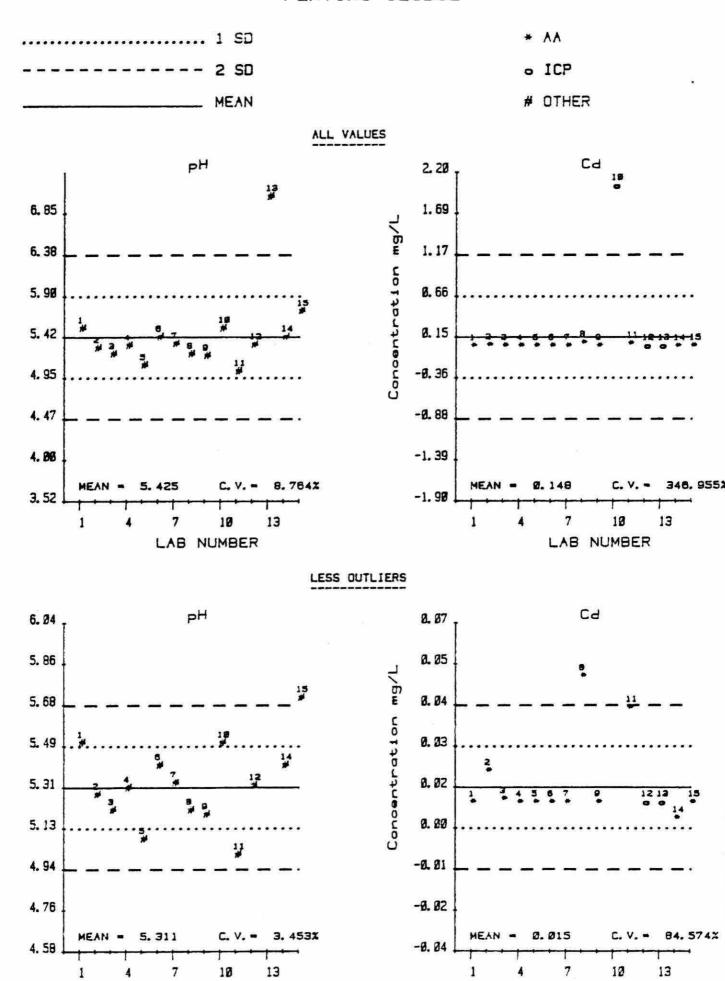
IRON FOUNDRY DUST



LESS OUTLIERS

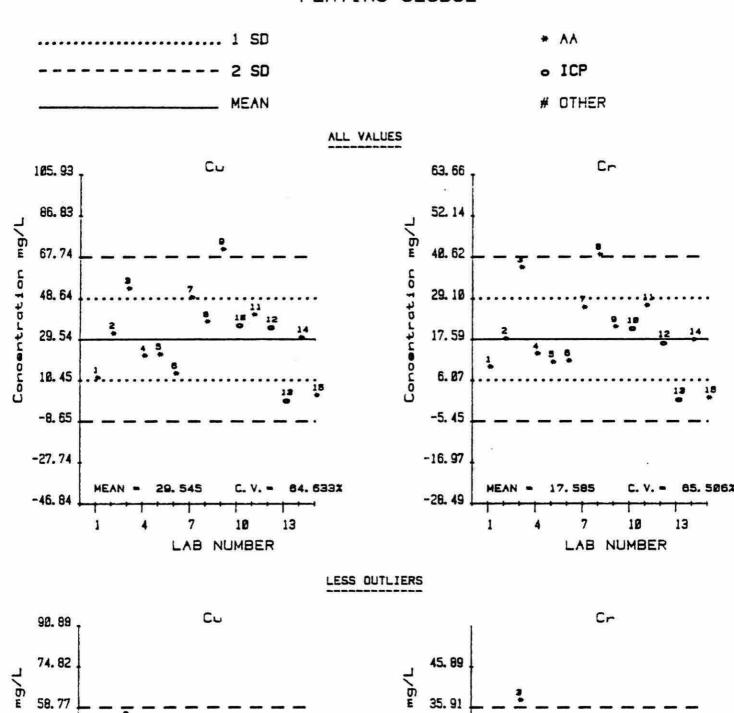


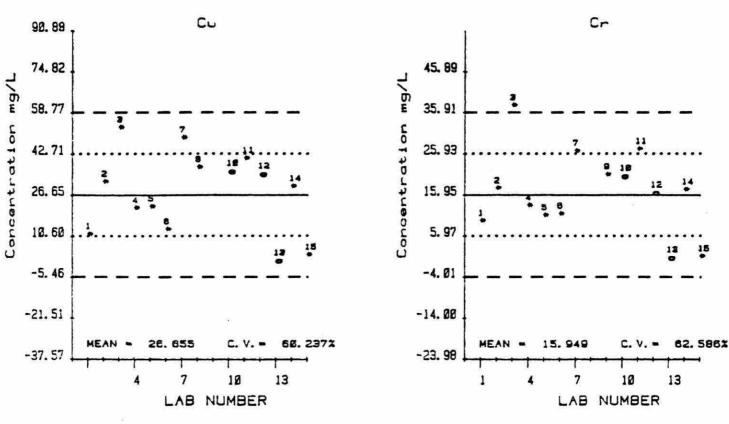




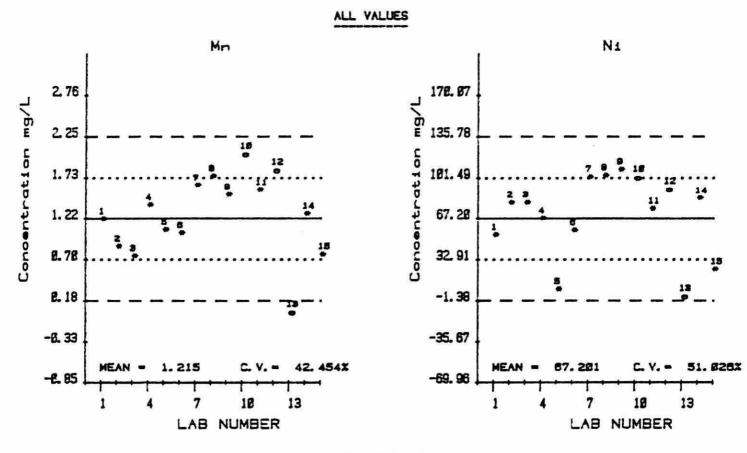
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LAB NUMBER

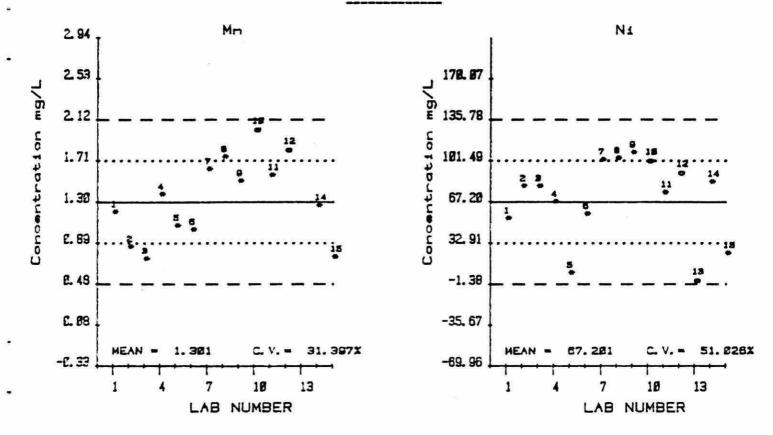


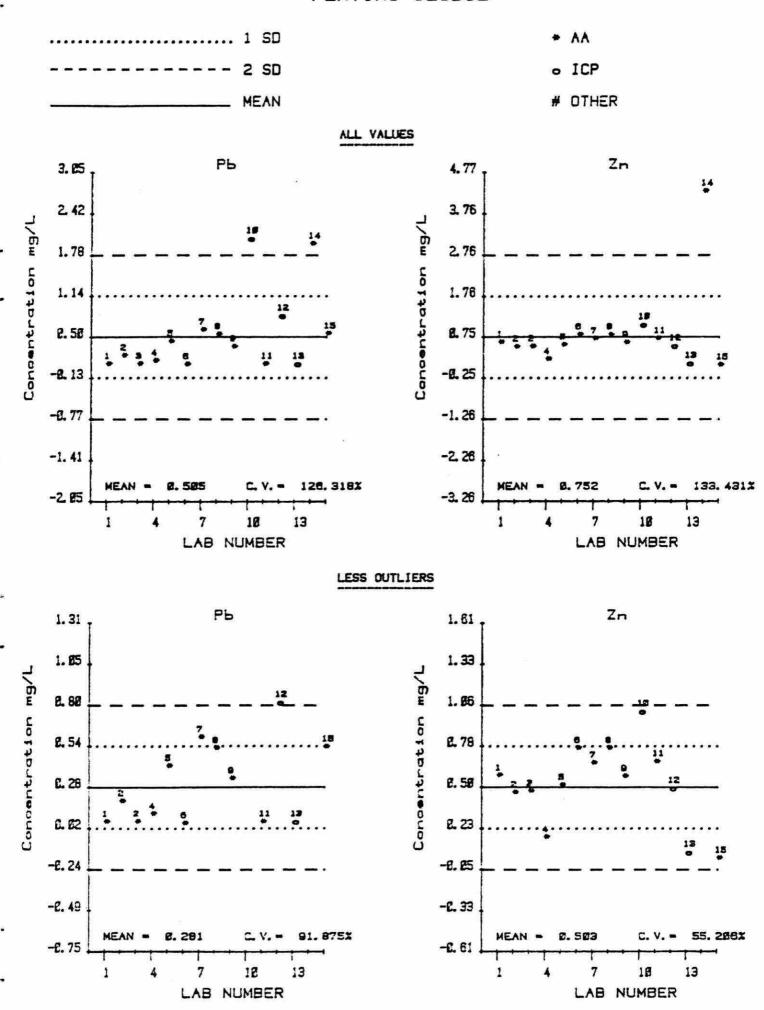






LESS OUTLIERS





APPENDIX A

Ontario Regulation 309

Leachate Extraction Procedure

THE DETERMINATION OF LEACHATE TOXICITY

SCOPE

The Leachate Extraction Procedure is intended primarily as a means for classifying wastes based on the leachability of contaminants in a waste material. A waste sample is treated with a dilute acetic acid solution, using a tumbler extraction technique, for a twenty-four hour period of time. The concentrations of contaminants in the leachate produced are measured and compared to the concentrations specified in the Waste Management Regulation.

Leachate containing concentrations less than one hundred times those specified in Schedule 4 of the Waste Management Regulation, classifies the waste as non-hazardous. Waste material, with leachate concentrations of contaminants equal to or greater than one hundred times those proscribed in Schedule 4, is classified as hazardous waste.

Although not required by the Regulation, this procedure may also be used to determine whether a waste can be used as a fill material on land. Leachate, using distilled water, for a landfill material shall not contain contaminant concentrations higher than those specified by a District Officer of the Ontario Ministry of the Environment. Criteria for fill material intended for disposal in open waters will be determined on an individual basis by the same authorities.

Wastes are normally extracted in their unaltered physical state, or if the aggregate particle size is greater than 9.5 mm, after comminution. Exceptions may be made for hard slag-like wastes or treated solidified wastes, which are likely to remain physically stable in a landfill site. The structural integrity procedure should be followed to determine if a particular waste requires comminution.

THE DETERMINATION OF LEACHATE TOXICITY

METHOD A. Leachate Extraction Procedure

(1) SAMPLING

Collect a sufficient amount of sample to provide approximately 100 g of solid material, using techniques which ensure that the sample is representative of the waste to be tested.

(2) EQUIPMENT

- 2.1 Sieve, 9.5 mm mesh opening, stainless steel or plastic material.
- 2.2 Stainless steel filtration unit, 142 mm diameter, minimum 1L capacity, capable of sustaining a pressure of 5 kg/cm², applied to the solution to be filtered.
- 2.3 Membrane filter, 142 mm diameter, 0.45 µm diameter pore size, made of synthetic organic material such as cellulose acetate, cellulose nitrate, nylon or polycarbonate and which is compatible with the leachate to be filtered. Teflon is recommended for organic constituents.
- 2.4 Glass fibre prefilter, 124 mm diameter, 3 um to 12 um pore size range
- 2.5 Vacuum filtration unit, 90 mm diameter.
- 2.6 Membrane filter 90 mm diameter as per Step 2.3.
- 2.7 Glass fibre filter 70 mm diameter as per Step 2.4.
- 2.8 Solid waste rotary extractor a device that rotates the bottles end overend about a central axis through 360 °, with a speed of 10 rpm.

The dimensions of the box will depend on the needs of each laboratory. (Figure 1).

- 2.9 Structural Integrity Tester with a 3.18 cm diameter hammer weighing 0.33 kilogram and having a free fall of 15.24 cm. (Figure 2).
- 2.10 pH meter, with a readability of 0.01 pH unit and accuracy of \pm 0.1 pH units.
- 2.11 Cylindrical bottles, wide mouth, 1250 mL capacity, polyethylene or glass with Teflon lined cap for inorganic constituents; glass with Teflon-lined cap or Teflon bottles for organic constituents.

2.12 Cleaning Procedure

All glassware and equipment that comes into contact with the sample should be cleaned in the following way before each use:

- 2.12.1 Wash with a non-phosphate detergent solution.
- 2.12.2 Rinse twice with tap water.
- 2.12.3 Rinse twice with reagent water.
- 2.12.4 Wash with 10% nitric acid.
- 2.12.5 Rinse several times with reagent water.
- 2.12.6 Store bottles filled with 10% nitric acid, until ready to use.
- 2.12.7 Rinse several times with reagent water before use.
- 2.12.8 Rinse clean oven dried bottles with methylene chloride, followed by methanol, for organic constituents.

(3) REAGENTS

- 3.1 Acetic acid, 0.5 N. Dilute 29.4 mL of concentrated acetic acid (ACS grade) to 1000 mL with reagent water.
- 3.2 Reagent water, Type IV (ASTM Specification D 1193). For organic parameters, the reagent water should be free of any organic substances to be analyzed (ASTM Type 1).
- 3.3 Nitric acid, 10% (v/v). Add 100 mL of concentrated nitric acid (ACS grade) to 900 mL of reagent water.
- 3.4 Nitrogen gas, prepurified, scrubbed through a molecular sieve.

(4) SEPARATION PROCEDURE

If the sample contains a distinct liquid and a solid phase, separate it into its component phases using the following procedure:

- 4.1 Determine the dry weight of the solids in the sample at 60 °C, using a well homogenised sample. Use this weight to determine the amount of material to be filtered in Step 4.8.
- 4.2 Assemble the filtration unit with a filter bed consisting of a 0.45 μm pore size membrane filter and a coarse glass fibre pre-filter upstream of the membrane filter (per manufacturer's instructions).
- 4.3 Select one or more blank filters from each batch of filters. Filter 50 mL portions of reagent water through each test filter and analyze the filtrate for the analytical parameters of interest. Note the volume required to reduce the blank values to acceptable levels, if necessary.
- 4.4 Wash each filter used in the leach procedure with at least this predetermined volume of water. Filter under pressure until no water flows through the filtrate outlet.

- 4.5 Remove the moist filter bed from the filtration unit and determine its weight to the nearest \pm 0.01 g.
- 4.6 Re-assemble the filtration unit, replacing the filter bed, as before.
- 4.7 Comminute the sample, with a mortar and pestle, to a size that will pass through the opening of the filtration unit (less than 9.5 mm).
- 4.8 Agitate the sample by hand and pour a representative aliquot of the solid and liquid phases into the opening of the filtration unit. Filter a sufficient amount of the sample to provide at least 60 g of dry solid material.
- 4.9 Pressurize the reservoir very slowly with nitrogen gas by means of the regulating valve on the nitrogen gas cylinder, until liquid begins to flow freely from the filtrate outlet.
- 4.10 Increase the pressure step-wise in increments of 0.5 kg/sq. cm to a maximum of 5 kg/sq. cm, as the flow diminishes. Continue filtration until the liquid flow ceases or the pressurizing gas begins to exit from the filtrate outlet of the filter unit.
- 4.11 De-pressurize the filtration unit slowly using the release valve on the filtration unit. Remove and weigh the solid material together with the filter bed to \pm 0.01 g. Record the weight of the solid material.
- 4.12 Measure and record the volume and pH of the liquid phase. Store the liquid at 4 °C under nitrogen until required in Step 5.13.
- 4.13 Discard the solid portion, if the weight is less than 0.5% (w/v) of the aliquot taken. If not, proceed to Step 5.1.

Note: For mixtures containing coarse grained solids, where separation can be performed without imposing a 5 kg/sq. cm differential pressure, a vacuum filtration unit with a filter bed as per Step 4.2 may be used. Vacuum filtration must not be used, if volatile organic compounds are to be analysed.

(5) EXTRACTION PROCEDURE

5.1 Prepare a solid sample for extraction by crushing, cutting or grinding, to pass through a 9.5 mm mesh sieve. If the original sample contains both liquid and solid phases, use the solid material from Step 4.13. The structural integrity procedure, Step 6 should be used for monolithic wastes which are expected to maintain their structural integrity in a landfill, (e.g. some slags and treated solidified wastes).

<u>Note:</u> Do not allow the solid waste material to dry prior to the extraction step.

- 5.2 Determine the moisture content of the de-watered sample, by drying a suitable aliquot to constant weight at 60 °C in an oven. Discard the dried solid material.
- 5.3 Place the equivalent of 50 g dry weight of the de-watered undried material into a 1250 mL wide mouth cylindrical bottle. Use additional bottles, if a larger volume of leachate is required for the analysis.
- 5.4 Add 800 mL (less the moisture content of the sample in mL) of reagent water to the bottle.
- 5.5 Cap the bottle and agitate it in the rotary extractor for 15 minutes before pH measurement.
- Measure and record the pH of the solution in the bottle using a pH meter, calibrated with buffers at pH 7.00 and pH 4.00. The solution should be stirred during the pH measurement.

- 5.7 Proceed to Step 5.10.1, if the pH is less than 5.2.
- 5.8 Add a sufficient volume of 0.5N acetic acid if the pH is greater than 5.2 to bring the pH to 5.0 + 0.2.
 - Note: Maximum Amount of Acid: No more than 4 mL of 0.5N acetic acid per gram of dry weight of sample may be added during the entire procedure. If the pH is not lowered to 5.0 ± 0.2 with this amount, proceed with the extraction.
- 5.9 Cap the bottle and place it in the tumbling apparatus. Rotate the bottle and its contents at 10 rpm for 24 hours at room temperature (20 °C to 25 °C).
- 5.10 Monitor, and manually adjust the pH during the course of the extraction, if it is greater than 5.0 ± 0.2 . The following procedure should be carefully followed:
 - 5.10.1 Measure the pH of the solution after 1 hour, 3 hours and 6 hours from the starting time. If the pH is above 5.2, reduce it to pH 5.0 ± 0.2 by addition of 0.5N acetic acid. If the pH is below 5.0 ± 0.2 , do not make any adjustments.
 - 5.10.2 Adjust the volume of the solution to 1000 mL with reagent water, if the pH is below 5.0 + 0.2 after 6 hours.
 - 5.10.3 Measure and reduce the pH to 5.0 \pm 0.2, if required, after 22 hours and continue the extraction for an additional 2 hours.
- 5.11 Add enough reagent water at the end of the extraction period so that the total volume of liquid is 1000 mL. Record the amount of acid added and the final pH of the solution.

5.12 Separate the material into its component liquid and solid phases as described under the Separation Procedure Step 4. Discard the solid portion.

<u>Note</u>: It may be necessary to centrifuge the suspension at high speed before filtration, for leachates containing very fine grained particles.

5.13 Calculate the amount of free liquid from Step 4.12 corresponding to 50 g of the dry solid material. Add this amount to the leachate from Step 5.12.

Note: If the analysis is not performed immediately, store separate aliquots of the leachate at 4 °C, after adding appropriate preservatives for the analytical parameters of interest (See "A Guide to the Collection and Submission of Samples for Laboratory Analysis", Ontario Ministry of the Environment, July 1979).

- 5.14 Analyze the combined solutions from Step 5.13 for contaminants listed in Schedule 4, that are likely to be present.
- 5.15 Report concentrations of contaminants in the combined leachate and the free liquid solution as mg/L.
- 5.16 Carry a blank sample through the entire procedure, using dilute acetic acid at pH 5.0 \pm 0.2.

6.0 STRUCTURAL INTEGRITY PROCEDURE

This procedure may be required prior to extraction for some samples as indicated in Step 5.1. It may be omitted for wastes with known high structural integrity.

Procedure

- 6.1 Fill the sample holder with the material to be tested. If the sample of the waste is a large monolithic block, cut a portion from the block measuring 3.3 cm in diameter by 7.1 cm in length. For a treated waste (e.g. solidified waste), samples may be cast in a form with the above dimensions for the purposes of conducting this test. In such cases, the waste should be allowed to cure for 30 days prior to further testing.
- 6.2 Place the sample holder in the structural integrity tester, then raise the hammer to its maximum height and allow it to fall. Repeat this procedure 14 times.
- 6.3 Remove the material from the sample holder, and proceed to Step 5.2. If the sample has not disintegrated, it may be sectioned; alternatively use the entire sample (after weighing) and a sufficiently large bottle as the extraction vessel. The volume of reagent water to be initially added is 16 mL/g of dry sample weight. The maximum amount of 0.5N acetic acid to be added is 4 mL/g of dry sample weight. The final volume of the leachate should be 20 mL/g of dry sample weight.

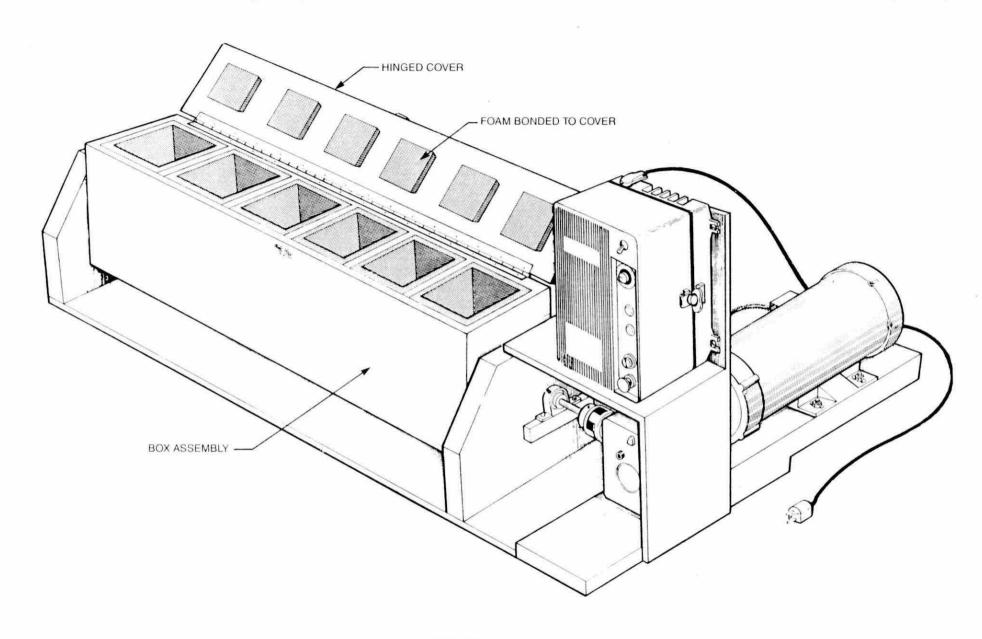


FIGURE 1 SOLID WASTE ROTARY EXTRACTOR

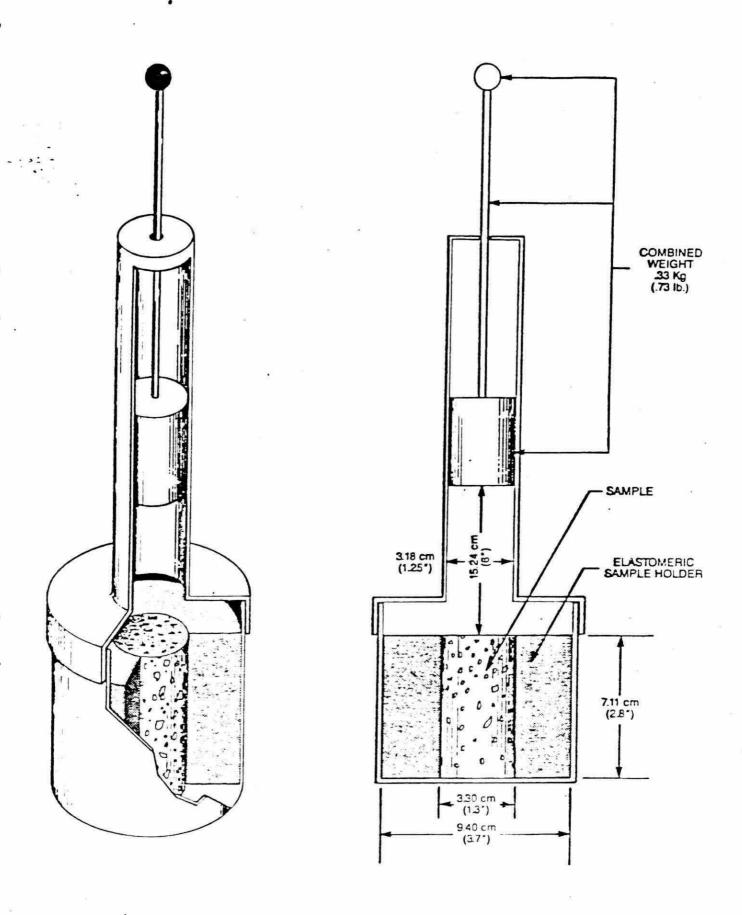


FIGURE 2 STRUCTURAL INTEGRITY TESTER

APPENDIX B

Reporting form for individual labs

MINISTRY OF THE ENVIRONMENT LABORATORY SERVICES BRANCH LEACHATE ANALYSIS COMPARATIVE STUDY, 1985

REPORTING SHEET

LABORATORY NAME:							INSTRUMENTATION: AAS ICP				
LABORATORY NUMBER:							OTHER (Please specify):				
DATE STARTED:											
DATE ANAL	LYSED:										
Sample	Sample Type	Initial pH	Final pH	Acid added mL	Cd	Cu	Cr	Mn mg/L	Ni	РЬ	Zn
Α	Smelting ESP dust										
В .	Coal Flyash										
С	Steel Flue Dust										
D	Iron Foundry Dust										
Е	Plating Sludge										
Blank	Distilled Water										
Reference solution:											

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